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JOURNAL ARTICLE

EFFECT OF SIMULATED SULFURIC ACID RAIN ON THE CHEMISTRY OF A SULFATE-ADSORBING FOREST SOIL

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Abstract. Simulated H_2SO_4 rain (pH 3.0, 3.5, 4.0) or control rain (pH 5.6) was applied for 3.5 yr to large lysimeter boxes containing a sulfate-adsorbing forest soil and either red alder (*Alnus rubra* Bong) or sugar maple (*Acer saccharum* Marsh.) seedlings. After removal of the plants and the litter layer, soil samples were obtained at 15-cm intervals to a total depth of 90 cm. Elevated SO_4 concentrations caused by the simulated H_2SO_4 rain were most pronounced for the top 15 cm, but extended down to 45 cm (maple) or 75 cm (alder). There were no effects on SO_4 concentrations at a depth of 75 to 90 cm. This confirmed the existence of a sulfate front between 20 cm and 100 cm, as postulated earlier on the basis of extracted soil solutions. Decreases in Mg and Ca concentrations, base saturation, and soil pH were limited to the uppermost 15 cm and, in most cases, to the pH 3.0 treatment. Concentrations of Mg and Ca for the pH 3.0 treatments were greater than control at a depth of 15 to 30 cm, indicating transport of these cations from the soil surface. Concentrations of Na and K, and cation exchange capacity, were not affected by simulated H_2SO_4 rain. Elevated concentrations of NO_3 and extractable Zn throughout the alder systems indicated (1) either increased rates of symbiotic N-fixation or decreased rates of N immobilization; and (2) mobilization of Zn by all acid rain treatments.

1. Introduction

Acidic deposition can, potentially, acidify unmanaged forest soils, leading to reduced productivity, tree mortality, and acidification of surface waters. However, there is no consensus as to whether the rate of acidification caused by acidic deposition is high enough to cause substantial adverse effects over a wide area within a few decades. The rate of acidification is thought to be controlled by soil factors such as cation exchange capacity (CEC), base saturation (or, alternatively, soil pH), presence or absence of carbonates, rate of mineral weathering, and anion (especially sulfate) mobility. The state of knowledge of the effects of acid deposition on soils has been reviewed recently (McFee *et al.*, 1983).

At EPA's Environmental Research Laboratory in Corvallis, Oregon, the effects of simulated H_2SO_4 rain on two types of model hardwood forest ecosystems were studied for 3.5 yr. An earlier report (Lee and Weber, 1982) reported changes in cation and sulfate concentrations in throughfall, litter leachate, and soil solutions. Acid rain was found to lower the pH and raise the concentrations of Ca, Mg, and K in soil solutions extracted from a depth of 20 cm. These changes were associated with increased SO_4 concentrations. However, no changes associated with acid rain occurred in solutions extracted from a depth of 100 cm. It was assumed that this was due to passage of a 'sulfate front' (i.e., region of saturation of sulfate adsorbing capacity) to a soil depth

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greater than 20 cm but less than 100 cm. This would be consistent with the 'mobile anion concept' of cation transport (Reuss, 1980; Johnson and Cole, 1980).

In this paper, I report on changes in the nutrient status of the soil caused by the simulated H_2SO_4 rain. The existence of a sulfate front at a depth consistent with the previously reported differences in the chemical composition of soil solutions is confirmed.

2. Methods and Materials

A detailed description of the model forest ecosystems is given by Lee and Weber (1982). Briefly, 18 water-tight enclosures (each 1.5 by 1.5 by 1.2 m) were filled to a depth of 1 m with a forest soil (Bohannon series of the fine-loamy, mixed, mesic family of typic Halpumbrepts). The soil horizons were reconstituted with respect to litter, topsoil, and subsoil layers. Each layer was mixed prior to being placed in the lysimeter boxes. Initial chemical analyses at the soil layers are given in Lee and Weber (1982). Soil water was extracted by applying a vacuum to porous ceramic samplers (Soil Moisture Equipment Corp.; Coors*) permanantly located within the soil profile. The ceramic samplers were leached with 1 N HCl prior to installation to minimize contamination. In 1975, nine of the plots were planted with sugar maple (*Acer saccharum* Marsh.) seedlings. The remaining nine plots were planted with red alder (*Alnus rubra* Bong) seedlings. Red alder was selected as an example of symbiotic N-fixation.

From June 1976 through January 1980, each plot, protected from ambient rain, received simulated acid rain at one of four acidities. There were two plots per treatment for each of the two tree species. The remaining two plots served as buffers. All experimental plots received a stock solution containing background ions approximating non-acidic rain (Lee and Weber, 1982). Control plots received the stock solutions, equilibrated with atmospheric CO_2 to pH 5.6. For the acid rain plots, the stock solution was acidified with H_2SO_4 to pH 4.0, 3.5 or 3.0. Simulated rain was sprayed from stainless steel nozzles (median mass diameter of droplets 1.2 mm) at a rate of 2.8 (maple) or 3.7 mm h^{-1} (alder) for 3 h day^{-1} and 3 days $week^{-1}$ throughout the year. Annual rainfall was 131 cm for maple and 173 cm for alder. These values were choosen to reflect differences in rainfall amounts between typical sugar maple and red alder stands; i.e. between the northeastern and northwestern U.S. Thus, total annual H^+ deposition on the maple plots was 0.03, 1.3, 4.1, and 13.1 keq ha^{-1} for the pH 5.6, 4.0, 3.5, and 3.0 treatments, respectively. Deposition on the alder plots was 32% greater due to the greater rainfall amount. By comparison, Johnson and Siccama (1983) estimate a total H^+ deposition rate of 2 to 3 keq $ha^{-1} \cdot y^{-1}$ for high elevations in the northern Appalachians, a region of high acid deposition. Deposition of background ions onto the maple plots from the stock solution was 0.8 kg ha^{-1} yr^{-1} Mg, 2.9 kg ha^{-1} yr^{-1} Ca, 1.6 kg ha^{-1} yr^{-1} Na, 1.1 kg ha^{-1} yr^{-1} K, 2.3 kg ha^{-1} yr^{-1} SO_4-S, 2.2 kg ha^{-1} yr^{-1} NO_3-N, 2.2 kg ha^{-1} yr^{-1} NH_3-N, 5.6 kg ha^{-1} yr^{-1} Cl.

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Application of simulated rain was initiated in June 1976 and terminated in January 1980. After removal of the above-ground portions of the trees and the litter layer, six soil cores were taken from each plot. Each core was 5 cm in diameter and driven to a depth of 90 cm. Due to soil compaction during coring, the cores were actually 70 to 75 cm long. Each core was divided into six equal segments corresponding to (approximately) 15-cm segments of soil depth within the lysimeters. After passing through a coarse fiberglass screen to separate out large roots and gravel, one-third of the sieved material from each segment was combined with material from the corresponding segments of the other five cores to produce a composite plot sample. Thus, for each plot, there were six composite samples, corresponding to six soil depths. The samples were analyzed for chemical content by the Soil Testing Laboratory at Oregon State University using methods summarized in Table I. Detailed descriptions and references for these

TABLE I

Methods used for soil analyses. Detailed descriptions and references are given in Kaufman and Gardner (1976)

Analyses	Method
pH	1:2 soil to solution ratio; pH of supernatant.
Mg	1N ammonium acetate extraction; atomic adsorption.
Ca	1N ammonium acetate extraction; atomic adsorption.
K	1N ammonium acetate extraction; atomic adsorption.
Na	1N ammonium acetate extraction; atomic adsorption.
BS[a]	Calculated as (Mg + Ca + Na + K)/CEC.
CEC[b]	1N ammonium acetate method.
Zn	DTPA method; atomic adsorption.
SO_4^{-2}-S	KCl extraction; methylene blue method.
NO_3^--N	Steam distillation method.
TN[c]	Micro-Kjeldahl method.
OM[d]	Walkley-Black titration method.

[a] Base saturation.
[b] Cation exchange capacity.
[c] Total N.
[d] Organic matter.

methods are given by Kaufman and Gardner (1976). Results were analyzed for species, depth and treatment effects and interactions using analysis of variance.

3. Results

The probability of Type-I error from the analysis of variance for each of the various effects and interactions is given in Table II. Table III gives the mean values of soil parameters which will be discussed on a treatment basis. These include parameters with statistically significant ($p \leq 0.05$) or possible ($p \leq 0.10$) treatment effects and/or inter-

TABLE II

Type-I probability values from analysis of variance of soil analysis

Effect	pH	Mg	Ca	K	Na	BS[a]	CEC[b]	Zn	SO_4^--S	NO_3^--N	TN[c]	OM[d]
Depth	0.0001	0.0001	0.0001	0.0048	0.0001	0.0001	0.001	0.0001	0.0001	0.0001	0.0001	0.0001
Species	0.10	0.58	0.97	0.0001	0.57	0.43	0.19	0.02	0.35	0.01	0.19	0.49
Treatment	0.63	0.71	0.58	0.25	0.78	0.19	0.43	0.04	0.0045	0.76	0.34	0.17
Depth × Species	0.0074	0.0001	0.0005	0.0001	0.02	0.0015	0.27	0.0033	0.05	0.0001	0.0001	0.0022
Depth × Treatment	0.0001	0.0044	0.07	0.78	0.42	0.06	0.73	0.61	0.0001	0.55	0.35	0.73
Species × Treatment	0.20	0.29	0.74	0.54	0.53	0.29	0.83	0.05	0.81	0.09	0.50	0.46
Depth × Species × Treatment	0.07	0.98	0.95	0.87	0.97	0.96	0.88	0.70	0.78	0.10	0.64	0.94

[a] Base saturation.
[b] Cation exchange capacity.
[c] Total N.
[d] Organic matter.

TABLE III

Results of soil analyses for which averaging over treatment is inappropriate. Alder and Maple refer to the tree species planted in the respective model ecosystems. BS refers to base saturation.

Depth (cm)	Treatment pH (Alder)				Treatment pH (Maple)			
	3.0	3.5	4.0	5.6	3.0	3.5	4.0	5.6
a. pH								
0–15	4.3	4.5	4.5	4.8	4.4	4.7	4.9	4.7
15–30	4.9	5.0	4.9	5.0	5.1	5.1	5.3	5.1
30–45	5.1	5.1	4.9	5.1	5.2	5.1	5.3	4.9
45–60	5.1	5.1	5.0	5.2	5.2	5.2	5.1	5.1
60–75	5.1	5.1	5.1	5.3	5.3	5.2	5.2	5.2
75–90	5.2	5.3	5.0	5.3	5.2	5.1	5.2	5.3
b. Mg (meq 100 g^{-1})								
0–15	0.34	0.47	0.55	0.55	0.32	0.50	0.57	0.56
15–30	0.72	0.89	0.69	0.73	1.10	1.15	1.03	0.93
30–45	0.95	0.75	0.67	0.68	0.93	0.71	0.83	0.75
45–60	0.84	0.74	0.60	0.72	0.68	0.61	0.59	0.63
60–75	0.77	0.96	0.80	1.05	0.75	0.74	0.83	0.85
75–90	0.89	1.00	0.88	0.96	0.84	0.86	0.89	0.87
c. Ca (meq 100 g^{-1})								
0–15	0.85	1.05	1.40	1.20	0.90	1.20	1.40	1.20
15–30	1.80	1.75	1.30	1.40	2.25	2.25	2.15	1.90
30–45	1.70	1.45	1.30	1.25	1.80	1.30	1.70	1.50
45–60	1.60	1.60	1.20	1.20	1.40	0.95	1.00	1.05
60–75	1.30	1.40	1.25	1.85	1.20	0.90	0.90	1.30
75–90	1.20	1.10	1.25	1.20	1.05	1.10	0.90	1.25
d. BS (%)								
0–15	6.2	6.8	8.1	7.8	5.9	7.9	8.8	8.0
15–30	11.1	11.4	8.9	9.3	14.6	12.7	13.4	12.3
30–45	12.5	10.6	9.1	9.9	12.6	9.4	11.5	10.6
45–60	14.5	15.1	10.0	12.2	12.7	10.1	9.3	10.7
60–75	14.2	15.6	12.5	18.3	12.8	10.4	11.7	15.2
75–90	14.2	13.0	14.2	14.0	12.7	12.9	12.3	13.5
e. Zn (mg kg^{-1})								
0–15	0.85	0.49	0.56	0.53	0.35	0.37	0.35	0.41
15–30	0.37	0.17	0.22	0.17	0.29	0.22	0.35	0.17
30–45	0.20	0.14	0.19	0.12	0.17	0.14	0.18	0.15
45–60	0.14	0.29	0.11	0.08	0.13	0.08	0.09	0.10
60–75	0.09	0.08	0.07	0.09	0.08	0.08	0.08	0.12
75–90	0.05	0.07	0.06	0.07	0.09	0.09	0.11	0.16
f. SO_4-S (mg kg^{-1})								
0–15	108.60	68.70	39.30	22.20	155.80	69.25	72.75	29.85
15–30	77.20	51.70	37.30	20.65	82.20	38.65	34.30	27.05
30–45	40.70	35.20	24.45	19.12	41.40	39.05	32.55	25.95
45–60	18.25	18.35	17.45	12.92	12.85	15.70	13.90	16.50
60–75	18.00	24.60	19.80	14.60	16.70	18.55	20.45	19.80
75–90	19.85	19.40	19.90	20.95	18.65	20.80	19.85	21.55
g. NO_3-N (mg kg^{-1})								
0–15	75.10	76.75	82.75	35.15	35.70	37.85	27.15	45.30
15–30	42.45	36.30	44.85	32.35	23.10	26.35	11.70	35.95
30–45	34.90	27.86	36.50	20.17	17.40	17.15	11.25	32.20
45–60	26.25	15.05	14.90	11.90	19.94	11.60	11.45	17.10
60–75	20.15	12.97	13.26	6.80	7.80	8.28	7.18	10.11
75–90	11.45	6.30	13.60	6.86	6.85	7.28	5.20	5.84

actions. Parameters for which there were no indication of a treatment effect or interaction, and which could be safely averaged over treatments, are given in Table IV.

The effect of depth was highly significant ($p \leq 0.005$) for all soil parameters (Table II). This was expected, since the 4.5 yr the soil was in the lysimeter boxes was not enough time to alter the original stratification of the soil. Thus, observation of differences with depth primarily serves as a test of adequacy of the sampling scheme and the statistical analysis. Because of the low p-values for depth effects, all the soil parameters are listed by depth in Tables III and IV.

Species and/or species × depth effects were significant for all parameters except CEC. The tendency for red alder to deplete basic cations, lower pH, and increase nitrate content of soils in natural stands has been documented by Franklin *et al.* (1968). They attributed these effects to rapid growth, high base content of wood, and symbiotic N fixation of alder. Similar effects occurred in the model ecosystems being discussed in this paper. Nitrate concentrations were generally higher in the alder ecosystems (Table IIIg). This was partly because the 147 cm of additional similated rain applied to the alder ecosystems during the 3.5 yr of the study deposited an extra 4.9 kg ha^{-1} of N in the forms of NH_3-N and NO_3-N. However, if this additional N was distributed over 1 m of soil, this would account for only an extra 0.5 mg at N per liter of soil; i.e. less than 0.5 mg kg^{-1} for a bulk density greater than 1.0. Therefore the differences were primarily due to symbiotic N fixation of alder. Base saturation was higher in the maple ecosystems to a depth of 45 cm, but higher in the alder ecosystems for depths of 45 to 90 cm. This indicates that the production of nitrate by symbiotic N fixation in the alder ecosystems resulted in a net transfer of basic cations (through leaching) from the uppermost soil layers to depths lower in the profile. Observation of species-effects indicates that the model ecosystems existed long enough for ecologically-driven soil differentiation to begin to be important.

The main focus of the study was the effect of the acid rain treatments on the nutrient status of soil. Treatment and/or depth × treatment effects were statistically significant for SO_4, pH, Mg and Zn and probable for Ca and base saturation. Also, marginally significant species × treatment and depth × species × treatment interactions occurred for NO_3 (Table II). These effects are discussed below.

The effects of the H_2SO_4 rain treatments on SO_4 concentrations in the soil were quite obvious (Table IIf). Elevated SO_4 concentrations were most pronounced for the top 15 cm, but extended down through 45 cm. Above 45 cm, soil-SO_4 concentrations followed a definite trend with rain pH; e.g., the highest soil-SO_4 concentrations were associated with the highest rain-SO_4 concentrations (lowest pH). For the alder ecosystems, the SO_4 concentrations at 45 to 75 cm for the controls were substantially lower than any of the corresponding values from the acid rain ecosystems. However, the soil-SO_4 concentrations did not follow a trend with rain-SO_4 concentrations. Thus, it appears that the sulfate status of the soil at a depth of 45 to 75 cm was just beginning to change in response to the simulated acid rain at the conclusion of the study. No effects of H_2SO_4 rain on SO_4 concentrations at 75 to 90 cm were evident for either maple or alder. The existence of a sulfate front extending past 20 cm, but not to 100 cm, as

postulated by Lee and Weber (1982) is confirmed. However, it is likely that at least in the alder systems, the sulfate front would have broken through to the bottom of the lysimeter boxes if the experiment had continued somewhat longer.

Simulated H_2SO_4 rain affected the base status of the soil, at least near the surface. Soil pH of the top 15 cm was lowered by the pH 3.0 treatment for both tree species (Table IIIa), and, to a lesser extent, by the pH 3.5 and 4.0 treatments in the alder ecosystems. Concentrations of Mg for the pH 3.0 treatments were lower than control for the top 15 cm of soil, but greater than control at a depth of 30 to 45 cm. Although the differences were not as significant (Table II), Ca and base saturation (Table IIIc and d) were affected similarly to Mg. Concentrations of K and Na, and cation exchange capacity (Table IV) were not affected by simulated H_2SO_4 rain (Table II). Thus, the net

TABLE IV

Results of soil analyses for which averaging over treatments is appropriate. Alder and Maple refer to tree species planted in the respective model ecosystems

Depth cm	Alder					Maple				
	K	Na	CEC[a]	TN[b]	OM[c]	K	Na	CEC[a]	TN[b]	OM[c]
	mg kg^{-1}	meq 100 g^{-1}		%	%	mg kg^{-1}	meq 100 g^{-1}		%	%
0–15	137.50	0.080	28.11	0.336	12.81	171.25	0.064	28.26	0.279	9.29
15–30	113.25	0.090	26.41	0.249	8.92	177.50	0.084	28.18	0.248	8.84
30–45	121.38	0.081	24.58	0.220	7.79	179.50	0.109	26.69	0.230	8.50
45–60	134.14	0.100	20.30	0.149	4.96	152.75	0.118	21.06	0.163	5.62
60–75	141.00	0.105	18.76	0.120	3.51	128.88	0.111	18.53	0.123	4.15
75–90	138.63	0.100	18.66	0.110	3.35	130.25	0.095	18.50	0.110	3.37

[a] Cation exchange capacity.
[b] Total N.
[c] Organic matter.

result of acid rai. was to transport Mg and Ca to deeper soil depths, with concomitant changes in base saturation. The point at which Mg and Ca accumulated appears to coincide with the point at which SO_4 was actively being removed from solution by adsorption. This is in agreement with the 'mobile anion' theory of cation transport (Johnson and Cole, 1977, 1980; Ruess, 1980).

There was an interactive effect of acid rain and tree species on Zn concentrations (Table II). The elevated concentrations of extractable Zn indicate that Zn was mobilized by acid rain in the alder ecosystems, but not in the maple ecosystems (Table IIIe). The effect was greatest for the pH 3.0 treatment and for the top 45 cm. However, for depths of 15 to 60 cm, concentrations of extractable Zn were higher than control for all acid rain treatments.

For the top 15 cm of the alder ecosystems, soil-NO_3 concentrations were substantially greater than control for all acid rain treatments. The tendency toward elevated NO_3 concentrations was observed for all treatments down to the lowest soil depths (0 to 90 cm), with only one exception (pH 3.5 at 75 to 90 cm). This could indicate either

increased rates of symbiotic N fixation, or decreased rates of N immobilization. However, because of the high *p*-values (i.e., marginal significance) for species × treatment and depth × species × treatment interactions (Table II), the existence of any effects on soil NO_3 is somewhat speculative. No acid rain effects on total-N or on organic matter were observed (Tables II and IV).

4. Discussion

The soil used in this study would generally be classified as insensitive to alterations in nutrient status by sulfuric acid rain (McFee *et al.*, 1983) because it is a strong sulfate adsorber throughout the profile (Johnson and Cole, 1977), and has a relatively high CEC, low base saturation, and low pH (Tables III, IV). Thus, the changes in nutrient status reported in this paper occurred in an (presumably) insensitive soil in the context of plant-soil interactions.

The experimental systems used in this study were simplified, and therefore imperfect, models of forest ecosystems. Most of the effects were limited to the most acidic treatment (pH 3.0). Total H^+ deposition for this treatment was approximately 4 to 8 times as great as occurs in the region of highest acid deposition (13-17 keq ha^{-1} vs 2 to 3 keq ha^{-1} as estimated by Johnson and Siccama, 1983), and perhaps ten times a rate typical of the northeastern U.S. Thus, although non-linearities in the system (Reuss, 1980) make extrapolation somewhat uncertain, it seems likely that similar changes could occur in 'insensitive' systems over a few decades (30 to 50 yr). This time-frame is not necessarily inconsistent with the concept of insensitivity, which is frequently defined in terms of changes in nutrient status of the top 25 cm of soil (e.g. McFee 1980). In this study, the adverse effects on soil pH and base saturation were limited to the uppermost 15 cm. However, increased concentrations of extractable Zn occurred to a depth of 60 cm in the alder ecosystems, indicating mobilization of at least one trace metal by acid rain throughout a substantial portion of the soil profile.

The possible effects of simulated acid rain on NO_3 concentrations in the alder ecosystems extended beyond the depth of the sulfate front. One possible explanation is that the effects on NO_3 were mediated by metabolic effects on the trees, which resulted in shifts in symbiotic N fixation and uptake in the rhizosphere. This would produce effects which extended throughout the root zone, but which were most pronounced in the region of greatest root density and activity, i.e., near the surface. This is precisely the pattern which was observed. It is conceivable that these same processes led to the mobilization of Zn in the alder ecosystems. This would not have occurred in the maple ecosystems, which lacked symbiotic N fixation. This would imply a complex interaction involving acid rain, plant response, N fixation, and trace-metal mobilization.

5. Conclusions

Lee and Weber (1982) used chemical analyses of soil solutions periodically extracted from these model ecosystems to conclude that:

(1) The sensitivities of the major cations to leaching by simulated H_2SO_4 rain were related by $Mg \geqq Ca > H > K$.
(2) Na was not sensitive to H_2SO_4 rain.
(3) In the model ecosystems which received acid rain, a sulfate-front had permeated to a depth greater than 20 cm but less than 100 cm.

These same conclusions are valid for the results presented in this paper, which are based on analyses of soil samples obtained at the end of the study.

In summary, acid deposition at rates typical of the most highly impacted region apparently can cause accelerated loss of bases in the top 15 cm of soil in some presumably 'insensitive' ecosystems. The ecological implications of these changes, which can occur over 30 to 50 yr, are not obvious. However, it should be noted that some locations in the northeastern U.S. have been subject to high rates of acid deposition for at least 30 yr. Also, some changes in trace metal mobilization and in N dynamics might occur over shorter time periods and to deeper depths.

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